### A. PROJECT MANAGEMENT

### **A1. Title and Approval Sheet**

# **U.S. Environmental Protection Agency Office of Research and Development Center for Environmental Measurement and Modeling**

Watershed & Ecosystem Characterization Division **Watershed Management Branch** 

## **Quality Assurance Project Plan**

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Title: QAPP FOR SURVEY OF RES	SERVOIR GREEI	NHOUSE GAS EMISSIO	NS (SuRGE)
QA C	Category: 🗆 A	⊠ B	
<b>ORD National Program Project/Task ID:</b> from surface water reservoirs for the U.		_	nane emissions
<b>QAPP was Developed:</b> ⊠ Intramurally	□ Extram	urally:	
QAPP Accessibility: QAPPs will be made int approval unless the following statement is sele		via the ORD QAPPs intran	<u>net site</u> upon final
$\square$ I do NOT want this QAPP internally sh	nared and acce	ssible on the ORD intra	anet site.
Project Type(s) (check all that apply):  ☑ Environmental Measurements ☐ Environment Informatics ☐ Geospatial ☐ Method Developme ☐ Software and Data Management ☐ Remote Se	ent 🗆 Model Appli	ication   Model Developm	=
Duamarad h	• •		
Prepared by: Dr. Jake J. Beaulieu			
	Signature		Date
Branch Chief: Dr. Michael Elovitz			
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<b>QA Manager:</b> Margie Vazquez			

Signature

Date

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QAPP Revision History				
QAPP ID Number Prepared By		Date of Revision	Description of Change	
J-WECD-0032592-QP-1-0	Jake Beaulieu	03/31/2020	Original QAPP.	

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#### A3. Distribution List

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### **A4. Project Organization**

**Project Technical Lead**: Dr. Jake Beaulieu (ORD/CEMM/WECD) will be the technical lead person for the project. His responsibilities include:

- Authoring and maintaining QAPP and relevant SOPs
- Generating overall survey design
- Generating survey designs for each waterbody.
- Serving as Contracting Officer Representative on Work Assignment / Task Order for Cincinnati on-site contract support.
- Coordinating project analytics (e.g., water chemistry) in AWBERC laboratories.
- Coordinating equipment needs among field crews.
- Ensuring that Field Crew Leads are exercising sufficient oversight over field activities.
- Data analysis and reporting

Field Crew Technical Lead: Field crews will be deployed from at least six geographic locations.

- Each field crew will have a technical lead whose responsibilities include:
  - Ensuring site access is coordinated with relevant governing authorities (e.g. private property owners, park managers) and that necessary permits/exemptions are obtained.
  - o Coordinating sampling schedule with Project Technical Lead.
  - Ensuring that field personnel adhere to procedures detailed in QAPP and SOPs
  - Oversee data management for sites sampled by their field crew.
- Field Crew Technical Leads are:
  - Cincinnati: Scott Jacobs (ORD/CESER/WID)
  - Narragansett: Jeff Hollister (ORD/CEMM/ACESD)
  - RTP: John Walker (ORD/CEMM/AESMD)
  - ADA: Ken Forshay (ORD/CESER/GCRD)
  - USGS: Bridget Deemer
  - R10: Lil Herger (USEPA/R10/LSASD)

Research Support Staff: Each Field Crew Technical Lead will be supported by 'Research Support Staff' who will be responsible for executing the procedures described in the QAPP and SOPs. Research Support Staff may vary from lake to lake, or year to year, but they must read and understand the QAPP and SOPs prior to contributing to the project. Research Support Staff should work in close coordination with Field Crew Technical Lead to ensure resources are coordinated appropriately and procedures are implemented in accordance with QA/QC documentation.

**Gas Lab Technical Lead:** Karen White (ORD/CEMM/WECD) will be the technical lead for the analysis of gas samples generated by the field crews. Responsibilities include:

- Evacuating and labeling gas vials for field sampling.
- Analyzing gas samples.
- Managing data from gas analyses.
- Submitting procurement requests for GC consumables.

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Water Chemistry Technical Leads: Each laboratory will have a water chemistry technical lead responsible for 1) ensuring that samples are received, stored, and analyzed according the relevant SOPs and QAPP, 2) ensuring that analytical data meet the relevant QA/QC criteria, or are flagged to indicate non-compliance, and 3) delivering the final data to the specified electronic repository (B.3.5 Electronic records).

- Cincinnati labs: Jake Beaulieu (ORD/CEMM/WECD)
- Ada labs: Ken Forshay (ORD/ CESER/GCRD)
- Narragansett labs: Jeff Hollister (ORD/ CEMM/ACESD)

**Quality Assurance Manager:** Margie Vazquez (ORD/CEMM/WECD) will provide independent quality assurance oversight to ensure that planning and plan implementation are in accordance with approved QAPP. The Quality Assurance Manager will provide technical direction from QA/QC perspective and will enter QAPP and all related products into ORD QA/QC databases.

### **A5. Problem Definition and Background**

Humans have built reservoirs for hydroelectric power generation, flood control, drinking water sources, and other uses. These man-made systems have provided society with important services, but these have come at the cost of enhanced greenhouse gas (GHG) emissions resulting from the biological production of carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), and nitrous oxide ( $N_2O$ ) in reservoir waters and sediments. The Intergovernmental Panel on Climate Change (IPCC) recently approved a methodology for including this emission source in national greenhouse gas inventories and the EPA's Office of Air and Radiation has requested ORD support in its implementation.

To reduce uncertainty in the inventory estimate, OAR has requested that ORD develop an empirically based emission factors for GHG emissions from U.S. reservoirs. Currently, there are insufficient data to develop an emission factor, therefore ORD and partners will conduct a national-scale survey of U.S. reservoirs during the summers of FY20 – FY22. This three-year field campaign will generate the data needed to define an empirically based emission factor allowing for an accurate and well constrained emission estimate for inclusion in the Inventory.

The primary work-product generated from this effort will be the data-set from the national-scale survey. The survey will not conclude until the end of the StRAP cycle (September 2022), however, and analysis, presentation, and publication of the data will be conducted under the FY23-26 StRAP. In the interim, ORD will develop a baseline estimate of methane emissions from U.S reservoirs using default IPCC emission factors. This baseline estimate will be revised during the FY19-22 StRAP as field data from the survey become available.

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### A6. Project/Task Description

	2019- 2020	2021	2022	2023	2023	2024
	Spring	Summer	Summer	Summer	Fall/Wint er	Winter/Spring
Activity						
Method						
develop						
ment/sur						
vey						
design						
Sample						
collection						
Data						
analysis						
Writing						

Table 1. Project schedule

### A7. Quality Objectives and Criteria for Measurement Data

The objective of the study is to estimate GHG emissions from U.S. reservoirs with a 95% confidence interval of +/- 25% of the estimated value. A power analysis using previously collected data suggested that approximately 100 measurement sites would be required to meet this criterion. The survey design includes 108 sites evenly allocated among the nine major U.S. ecoregions.

### **A8. Special Training/Certifications**

In April 2020, the Project Technical Lead will provide training on the sampling methodologies for Field Crew Technical Leads and Research Support Staff. The Project Technical Lead, or an experienced Field Crew Technical Lead, will also conduct site visits to provide additional on-site training and oversight.

Boat operators may be required to receive training from the relevant state agency (i.e. Ohio Department of Natural Resources). The Field Crew Technical should verify the state requirements for their sampling area. Electronic copies of the certificates will be stored at the SuRGE Sharepoint documents library: "Environmental Protection Agency (EPA)\SuRGE Survey of Reservoir Greenhouse gas Emissions - Documents\projectDocuments\training certificates"

#### **A9. Documents and Records**

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Paper records will be generated per the data sheets in section F. Appendix. Paper and electronic

records will be managed as specified in B.3.4 Paper records and B.3.5 Electronic records.

### **B. DATA GENERATION AND ACQUISITION**

### **B1.** Experimental Design

### B1.1 Survey design

The objective of the research is to estimate the magnitude of GHG emissions from U.S. reservoirs. Accomplishing this via classical survey design principles requires 1) a definitive list of all U.S. reservoirs (the 'sample frame'), and 2) a probabilistic subset of the sample frame for sampling. No definitive list of U.S. reservoirs exists, however, so the sample frame for SuRGE is defined as the 522 reservoirs sampled in EPA's 2017 National Lakes Assessment (NLA). The NLA is a probabilistic survey of all U.S. waterbodies > 1 Ha included in the USGS National Hydrography Dataset (NHDPlusV2). The subset of NLA sites that are confirmed to be reservoirs by the field crews therefore represent a probabilistic subset of all U.S. reservoirs. This property of the NLA sampled reservoirs will allow us to estimate GHG emissions for all U.S. reservoirs by making detailed measurements at a subset of the NLA reservoirs.

Upscaling measurements to the nation can also be accomplished via statistical modeling based on environmental drivers that control emission rates. To ensure variation in potential environmental drivers across the reservoirs, and to ensure national-scale coverage, the survey design entails stratification by ecoregion, chlorophyll a, and depth. Twelve sites are distributed within each of the 9 major U.S. ecoregions, for a total of 108 sample sites. Reservoirs are further classified as high or low chlorophyll (> or < 7 ug/L, respectively) and deep or shallow (< or < 6m, respectively), creating four unique combinations of depth and chlorophyll. Within each ecoregion, three sites are apportioned to each of these four combinations. The survey design also includes 'oversample' sites which can be used to replace main sites that are inaccessible due to landowner denial, lack of physical access, or other reasons.

The 108 reservoirs (Figure 1) will be sampled one-time between June 1 and Sept. 15 of 2020, 2021, or 2022. Within each reservoir, sampling will consist of measurements of diffusive and ebullitive emissions at ≥15 sites. Water chemistry will be sampled at the site where we anticipate the greatest depth, defined as the 'Index Site'. Larger, or highly dendritic reservoirs, may be broken into several sections. This is done to ensure that Oversample sites, when needed, are always within a reasonable distance of the target site that is being replaced. The location of the sampling sites will be defined using a Generalized Random Tessellation Stratified (GRTS) survey design.



Figure 1. Location of 108 reservoirs to be sampled during SuRGE.

#### **B1.2** Process measurement

#### *B1.2.1 Ebullition rates*

We will measure ebullition rates during the survey using inverted funnels deployed from a buoy. The funnels intercept rising gas bubbles which collect in a reservoir attached to the top of the funnel. After a minimum 12 hour deployment period, the volume of gas in the trap will be measured and subsampled for analysis of methane, carbon dioxide, nitrous oxide, oxygen, nitrogen, and argon. See SOP# J-WECD-WMB-SOP-3948-0 'Measurement of Ebullition Rates using Passive Gas Traps'. The SOP is available at the ORD intranet site and in the SuRGE documents library at **SharePoint**.

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#### B1.2.2 Diffusive emissions via floating chambers

Diffusive emission rates will be measured at each site using a floating chamber (Figure 2) interfaced to a portable greenhouse gas analyzer.

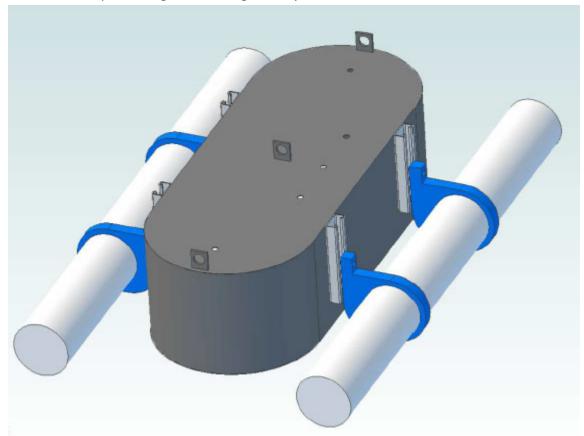


Figure 2. Three dimensional drawing of floating chamber that will be used for measuring diffusive emission rates.

#### *B1.2.3 Sonde measurements*

Water temperature, specific conductivity, dissolved oxygen, pH, turbidity, and chlorophyll will be measured using a multiparameter sonde ~0.1m below the water surface at all sites, 0.5m above the sediments at sampling sites >1 and < 4 m deep, and 1 m above the sediments at sites > 4 m deep. The same variables will be measured throughout the water column at the Index Site (B2.4 Sonde measurements).

#### B1.2.4 Water chemistry and algae indicators

Water chemistry and algae indicators will be collected at the Index Site. Both sample types will be collected from a depth of ~ 0.1 m. Water chemistry will also be collected from the bottom waters at sites > 1m deep using a Van Dorn bottle, or equivalent. Water chemistry samples will be analyzed for dissolved nitrite + nitrate (NO<sub>2,3</sub>), dissolved ammonium (NH<sub>4</sub><sup>+</sup>), dissolved reactive phosphorus (DRP), dissolved metals, total organic carbon (TOC), total phosphorus (TP), and total nitrogen (TN). Algae indicators are chlorophyll a, phycocyanin, and microcystin.

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#### B1.2.5 Dissolved gas samples

Triplicate dissolved gas samples will be collected from 0.1m below the water surface at the Index Site and 0.5 m above the sediments at Index sites < 4 m deep or 1 m above the sediments at Index sites > 4 m deep. Sampling procedure will follow SOP SuRGE Dissolved Gas Sampling and samples will be analyzed for CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub>.

#### B1.2.6 Air samples

Triplicate air samples will be collected approximately 2m above the air-water interface at the Index site per SOP SuRGE Dissolved Gas Sampling.

#### **B1.3** Photos

Field crews are encouraged to collect photos that could be useful for reconstructing conditions during the survey including weather conditions (e.g. rainy, cloudy, sunny), shoreline development patterns (e.g. forested shoreline or crowded with vacation homes), and water quality (e.g. clear water or green with algae!). Field crews are required to take two photos at the Index Site. The first photo will be of the passive gas trap deployed in the lake. This image should be taken with the boat positioned with 10 feet of the buoy and include the passive trap buoy. This image will provide an indication of water clarity. The second image is intended to give some sense of the size of the waterbody and shoreline conditions. It will be taken at the Index Site with camera pointed along the longest stretch of water unbroken by the shoreline. The file names for these images will be indexLakexxx.jpg and indexTrapxx.jpg for the lake and trap images, respectively, where XXX is the three-digit numeric component of the siteID field in the SuRGE survey design file. This file can be accessed through the web app, the SuRGE GeoPlatform group, and the SuRGE documents library at SharePoint. Most cameras will generate .jpg images, but other formats (e.g., .tiff) are acceptable.

#### B1.4 General approach and test conditions

GHG emission rates are likely to vary in response to numerous drivers including extreme water levels (high or low), rapidly changing water levels, and unusually high inflow rates. This variability is real and should be reflected in our measurements. Therefore, field crews should be prepared to sample across a broad range of conditions, unless the conditions affect safety (e.g. lightning storms) or accessibility (e.g. reservoir is dry due to extreme drought).

The sampling activities can be distributed across two days at the discretion of the Field Crew Technical Lead. However, the following groups of samples must be collected at the same time from any one particular site:

- Group 1: floating chamber measurements, air samples, shallow water temperature, and shallow dissolved gases.
- Group 2: algal indicators (chlorophyll, phycocyanin, and microcystin).
- Group 3: deep and shallow sonde measurements

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The remaining measurements can be distributed across days 1 and 2 at the discretion of the Field Crew Technical Lead. Example work distributions include:

#### Example 1

- Day 1: deploy passive gas traps, floating chamber measurements, deep and shallow sonde measurements, water chemistry, gases, algal indicators, Index Site depth profile
- Day 2: retrieve passive gas traps

#### Example 2

- Day 1: deploy passive gas traps, floating chamber measurements, deep and shallow sonde measurements, shallow dissolved gases, and air
- Day 2: retrieve passive gas traps, deep and shallow water chemistry, deep dissolved gases, algal indicators, Index Site depth profile

#### • Example 3

- Day 1: deploy gas traps, deep and shallow water chemistry, algal indicators, deep dissolved gas, Index Site depth profile
- Day 2: retrieve passive gas traps, floating chamber measurements, deep and shallow sonde measurements, shallow dissolved gas, air samples

#### Example 4

- Day 1: deploy passive gas traps, deep and shallow sonde measurements, Index Site depth profile, deep and shallow water chemistry, algal indicators, deep dissolved gas
- Day 2: retrieve passive gas traps, floating chamber measurements, shallow water temperature (see F3. Surge Greenhouse gas analyzer and gps data sheet), shallow dissolved gas, air samples

### **B2. Sampling Methods**

#### **B2.1** Site specific factors

#### B2.1.1 Lake evaluation

Field Crew Technical Leads will be provided a list of Target and Oversample lakes. Prior to sampling, the Field Crew Technical Lead must determine if it is logistically possible to sample the Target lakes. This evaluation will be based on factors including accessibility (e.g., can the lake be reached by road, can a boat be launched in the lake), property rights (e.g., landowner denial), and lake-specific restrictions (e.g., no boats allowed on drinking water reservoirs). If a Target lake cannot be sampled, it must be replaced with the first oversample lake within the same stratum. If no oversample lakes are available for the stratum, choose from a different stratum within the same ecoregion.

Lake evaluation status must be recorded at "SuRGE Survey of Reservoir Greenhouse gas Emissions - Documents\surgeDsn\SuRGE\_design\_20191206\_eval\_status.xlsx" at the <a href="SharePoint">SharePoint</a> site. Choices for Eval Status Codes include 'LD' (land owner denial), 'PI' (physically inaccessible;

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no road access, no boat ramp, or no water due to dam maintenance), 'TR' (too remote, extreme effort required), and 'S' (sampleable, no barrier to site access).

#### B2.1.2 Sample site evaluation

The Field Crew Technical Lead will be provided with a map of the anticipated sampling locations (electronic version and hardcopy) for each reservoir. For each sampling location an Evaluation Code must be recorded in F1. SuRGE SAMPLING EVENT SUMMARY. Acceptable entries for the Evaluation Code are TS (Target Sampled), PI (Physically inaccessible), NT (Non-Target), and NS (Target Not Sampled). TS applies to sites where no problem is encountered and the sampling proceeds as normal. Examples of PI include sites that are too shallow to access, are roped off (as is often done near dams), or a low bridge prevents access. NT applies to sites that are not within the reservoir. This can occur when the GIS shapefile isn't accurate, typically near the shorelines. NS applies to target sites that were not sampled. This might occur if the field crew runs out of time to complete the sampling or if there were problems with the sampling equipment (e.g., vandalized funnels or malfunctioning portable greenhouse gas analyzer).

Sites that have an evaluation code of PI or NT must be replaced with sites from the Oversample list. The Oversample list is a list of extra sites that can be used to replace target sites, while preserving the statistical integrity of the survey. Oversample sites must be drawn in order from the top to the bottom of the list. If the lake survey design includes sections, then each section will have a unique oversample list. This ensures that Oversample sites, when needed, are within a reasonable distance of the target site that is being replaced.

#### B2.2 Ebullition rates and gas composition

Ebullition rates will be measured using overnight passive gas trap deployments (> 14 hours) as described in SOP# J-WECD-WMB-SOP-3948-0 'Measurement of Ebullition Rates using Passive Gas Traps'. The SOP is available at the <u>ORD intranet site</u> and in the SuRGE documents library at <u>SharePoint</u>. See F2. Surge GAS TRAP DATA SHEET for data sheet.

#### B2.3 Diffusive emissions via floating chambers

Methane and carbon dioxide emission rates will be measured using a version of the floating chamber technique [Livingston and Hutchinson]. This method consists of trapping a parcel of air between the surface of the lake and a floating chamber and monitoring how rapidly the composition of the headspace gas changes.

Headspace gas composition will be monitored in real time using a portable greenhouse gas analyzer which will continuously recirculate the chamber headspace and measure  $CH_4$  and  $CO_2$  concentrations every 10 seconds and store the data on an internal solid state harddrive. The Cincinnati and RTP field crews may use a Picarro G2508, Los Gatos UGGA, or Los Gatos MGGA. All other field crews will use a Los Gatos instrument. The Picarro instrument also records nitrous oxide  $(N_2O)$  concentrations.

When the portable greenhouse gas analyzer is turned on, the performance specifications in Table 2 should be checked against the instrument readout. See user manuals at the SuRGE documents library at <a href="SharePoint">SharePoint</a> for operational details.

Measurement	Plausible values
Picarro and LGR specs	
Ambient CH₄	1.8 – 3.0 ppm
Ambient CO <sub>2</sub>	350 – 450ppm
LGR UGGA specs	
Cell temperature	Near ambient (15 – 30C)
Cell pressure	139 -141 Torr
Laser a τ	30
Laser b τ	35
Picarro G2508 specs	
Ambient N₂O	300 – 320 ppb
N <sub>2</sub> O precision	TBD
CO <sub>2</sub> precision	TBD
CH <sub>4</sub> precision	TBD
Measurement Interval	2-6 (1 point / 2-6 seconds)

Table 2. Performance specifications for greenhouse gas analyzers.

The floating chamber will consist of an aluminum chamber (20 cm height x 74 cm length x 30 cm width; Figure 2) equipped with removable floats, a small fan for mixing the chamber headspace, and two  $\frac{1}{4}$ " Swagelok sampling ports. The sampling ports will be interfaced to 1 m lengths of polytetrafluoroethylene tubing ( $\frac{1}{4}$ " O.D.) connected to the portable greenhouse gas analyzer.

The floating chamber will be carefully lowered to the water surface and deployed for a minimum of 2 minutes at each site. The boat should be allowed to drift during deployment and the location recorded continuously with the provided GPS unit (or equivalent). The gas analyzer data will be viewed in real-time via a ruggedized monitor hardwired to analyzer (Picarro) or a tablet/computer interfaced to the LGR via a wireless connection. The field analyst will immediately preview the data to ensure that an acceptable emission profile was captured. An acceptable emission profile will be characterized by  $CH_4$  and  $CO_2$  concentrations that smoothly increase or decrease for at least 2 minutes. If the chamber happens to capture a rising bubble, the constant rate of change will be interrupted by an abrupt increase in  $CH_4$  concentration. Increases of < 0.5ppm  $CH_4$  can be ignored, but the chamber will need to be vented and the deployment repeated if the concentration jump exceeds 0.5 ppm  $CH_4$ . This includes moving the boat back to the sampling site and allowing  $CH_4$  and  $CO_2$  concentrations to return to background levels.

Methane emission profiles characterized by concentration measurements that exhibit no temporal trend are also unacceptable. This can occur is the chamber headspace is not well mixed or the chamber is leaking. It is plausible for CO<sub>2</sub> to exhibit a flat concentration when dissolved CO<sub>2</sub> and O<sub>2</sub> are near equilibrium. The CO<sub>2</sub> profile should show increasing concentrations if dissolved oxygen (DO) is undersaturated and falling concentrations if DO is undersaturated.

#### **B2.4 Sonde measurements**

Water temperature, specific conductivity, dissolved oxygen, pH, turbidity, and chlorophyll will be measured using a multiparameter sonde 0.1 m below the water surface at all sites and 0.5 m above the sediments at sampling sites < 4 m deep and 1 m above the sediments at sites > 4 m deep (Table 3).

Site Depth	Depth for 'deep' water chemistry samples and sonde measurements
<=1 m	No 'deep' measurement
>1 m and <4 m	0.5 m above sediment
>4 m	1.0 m above sediment

Table 3. Sample depths for deep water chemistry samples and sonde measurements.

A full depth profile will be measured at the Index Site. The shallowest measurement will always be 0.1m below the water surface. Subsequent measurement intervals are based on site depth according to Table 4.

Index Site Depth	Measurement interval
<4m	Record measurements beginning just below the surface and at 0.5 m intervals, until 0.5 m above the bottom.
>=4m & <= 20m	Record measurements beginning just below the surface and then at 1.0 m intervals until reaching 1 m above the bottom.
>20m	Record measurements beginning just below the surface, then at 1.0 m intervals until you reach 20 m, then at 2.0 m intervals until 1.0 m above the bottom.

Table 4. Index Site depth profile measurement intervals.

Measurements will be made by lowering the sonde to the desired depth and allowing the values to stabilize. Values are typically stable when they no longer show directional drift. Water temperature typically stabilizes first with values varying by no more than ±0.1 °C. Other parameters may take longer to stabilize. Index Site depth profiles will be recorded in Appendix F4. Surge sonde data sheet for index site depth profile. All other sonde measurements will be recorded in Appendix F5. Surge sonde data sheet for deep and shallow **MEASUREMENTS** 

#### B2.5 Water chemistry and algal indicators

#### B2.5.1 Sample site and depths

Water chemistry and algal indicator samples will be collected at the Index Site. Both sample types will be collected from a depth of  $\sim 0.1$  m. Water chemistry will also be collected from the bottom waters using a Van Dorn bottle, or equivalent. See Table 3 for sample collection depth.

#### B2.5.2 Water chemistry and algal indicator sampling

Water chemistry and algal indicator samples will be analyzed for the analytes in Table 5. Below is the step by step procedure for collecting these samples. See Figure 3 sampling flow chart.

- 1. **Shallow** dissolved nutrients and dissolved metals.
  - a. Rinse an acid washed 140 mL syringe three times with water collected from just below the water surface, avoiding any surface scum.
  - b. Pull 140 mL of water into syringe and attach a GD/XP filter.
  - c. Rinse the filter by pushing ~20 mL of water through filter. The filtrate should be discarded.
  - d. Rinse the prelabeled 30 mL dissolved nutrient and 60 mL dissolved metals bottle with  $\sim \! 10$  mL of filtered site water. The dissolved metals sample will be acidified in Cincinnati lab.
  - e. Fill the prelabeled 30 mL dissolved nutrient and 60 mL dissolved metals bottle to just below the shoulder with filtered site water.
  - f. Place the samples on ice.
- 2. **Shallow** total nutrients, total organic carbon, microcystin, phycocyanin, and chlorophyll
  - a. Rinse the prelabeled 30 mL total nutrient vial, 20 mL microcystin vial, 1 L chlorophyll bottle, and 1 L phycocyanin bottle with site water three times. DO NOT rinse pre-acidified TOC vial.
  - b. Fill bottles to just below the shoulder with site water for all vials <u>except</u> the 20 mL microcystin vial. For the 20 mL microcystin vial, fill with site water from phycocyanin bottle and fill to ~2/3 total volume to allow for expansion due to freezing.
  - c. Fill the pre-acidified and prelabeled 40 mL TOC vial with site water from the 1L chlorophyll bottle. Cap the TOC vial, ensuring no headspace.
  - d. Place all samples on ice.
- 3. **Deep** dissolved nutrients, dissolved metals, total nutrients, total organic carbon.
  - a. Bottom water samples are collected using a Van Dorn bottle, or equivalent.
    - i. Lower Van Dorn bottle, or equivalent, to the sampling depth (Table 3).
      - 1. If using a vertical sampler, drop the messenger and retrieve bottle.
      - If using a horizontal sampler, displace the bottle horizontally
         ~2 m to capture an undisturbed portion of the water column.
         Drop the messenger and retrieve the bottle.
  - b. Process the samples per steps 1 and 2 above, except that the water is collected from the Van Dorn bottle, or equivalent. The same syringe and filter can be used for both depths, provided steps 1a-d above are followed.
  - c. Place all samples on ice.

### B2.5.3 Chlorophyll and phycocyanin sample processing

The chlorophyll and phycocyanin water sample must be filtered and frozen for chlorophyll and phycocyanin analysis within 24 hours. Homogenize the sample (i.e., shake, not stir) and vacuum filter in 50 mL aliquots across a 0.7µm glass fiber filter until 800 mL has been filtered or the filter becomes clogged. The vacuum pressure must not exceed 6 in. Hg (20 kPa) during filtration. Use squeeze bottle (Base Kit, F8. Surge EQUIPMENT AND SUPPLIES) and deionized water (Field Crew Supplied Items; F8. Surge EQUIPMENT AND SUPPLIES) to rinse particles clinging to the walls of the graduated cylinder and filter tower onto the filter. Be certain to record the total volume of water filtered (excluding deionized water) in Appendix F6. SuRGE CHLOROPHYLL/PHYCOCYANIN SAMPLE PREP DATA SHEET. Use a tweezer to fold the filter in half with the filtrate on the inside, then wrap the filter in foil, place in a ziplock bag, and freeze in standard commercial freezer until filters are shipped.

The 1L water sample bottles for chlorophyll and phycocyanin may be re-used between sites on a single sampling outing. Wash each bottle out with copious amounts of tap water (e.g. hotel sink) after each sample collection. Prior to sample collection, fill, shake and empty bottles three times prior to collecting sample in the field. Upon returning from the field, acid wash bottles in preparation for next sampling outing.

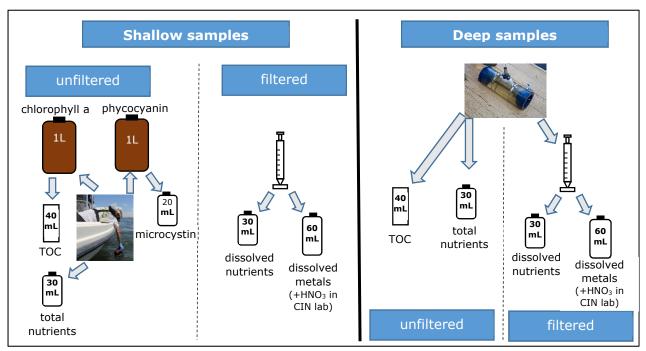


Figure 3. Flow chart for processing water samples.

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#### B2.6 Gases

#### *B2.6.1 Dissolved gases*

Triplicate dissolved gas samples will be collected from the minimum depth required to keep syringe stopcock submerged during sampling (~0.1 m), and from bottom waters (see Table 3 for sampling depth) at the Index Site. Samples will be collected in 140 mL syringes following SOP# J-WECD-WMB-SOP-3948-0 'SuRGE Dissolved Gas Sampling' available at the ORD intranet site and in the SuRGE documents library at SharePoint. Record the sampling details in Appendix F7. SuRGE DISSOLVED GAS AND AIR DATA SHEET.

#### B2.6.2 Air samples

Triplicate 20 mL air samples will be collected from ~ 2m above the water surface at the Index Site using a 30 mL syringe per SOP# J-WECD-WMB-SOP-3948-0 'SuRGE Dissolved Gas Sampling' available at the ORD intranet site and in the SuRGE documents library at SharePoint. Air temperature should also be measured. Record the sampling details in Appendix F7. SuRGE DISSOLVED GAS AND AIR DATA SHEET.

#### B2.7 Sample containers and quantities

#### See section

DISSOLVED METALS ANALYTES	DETECTION
(Method: EPA 200.8)	LIMIT, μg/L
(Al) Aluminum	<mark>-0.004</mark>
(As) Arsenic	-0.004
(Ba) Barium	-0.001
(Be) Beryllium	-0.005
(CA) Calcium	<mark>-0.01</mark>
(Cd) Cadmium	-0.0003
(Cr) Chromium	-0.001
(Cu) Copper	-0.001
(Fe) Iron	-0.001
(K) Potassium	<mark>-0.3</mark>
(Li) Lithium	-0.005
(Mg) Magnesium	<mark>-0.005</mark>
(Mn) Manganese	-0.001
(Na) Sodium	<mark>-0.03</mark>
(Ni) Nickel	<mark>-0.001</mark>
(Pb) Lead	-0.002
(P) Phosphorus	-0.005
(Sb) Antimony	-0.003

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(Si) Silicon	-0.02
(Sn) Tin	-0.001
(Sr) Strontium	-0.001
(S) Sulfur	-0.003
(V) Vanadium	-0.001
(Zn) Zinc	-0.0005

Table 7. Instrument dissolved metals analyte list: highlighted analytes are of interest for SuRGE project.

### B5. Quality Control for details on numbers of QA/QC samples.

Analyte Group	Analyte	Filtered or unfiltered	Container and volume	Total number of samples	Preservation	Holding times
Group	Dissolved	ummerea	volume	samples	Preservation	umes
	Nutrients  NO <sub>2.3</sub> NH <sub>4</sub> <sup>+</sup> reactive P	Filtered	30 mL HDPE	2 per lake + QA/QC Total = ~240	24 hours @ 5°0 at -20	•
Water chemistry	Total Nutrients  TP  TN	Unfiltered	30 mL HDPE	2 per lake + QA/QC total = ~240	24 hours @ 5°0 at -20	
	тос	Unfiltered	40mL TOC vial	2 per lake + QA/QC total = ~240	4°C + 2 drops 50% HCl in field	28 days
	Dissolved metals	Filtered	60 mL HDPE bottle	2 per lake + QA/QC total = ~240	3 drops 2% HNO₃ in CIN lab	60 days
	Dissolved N <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub>			6 per lake total = 648		
Gases	Gas trap N <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub>	12mL glass vial		≤45 per lake Total ≤ 4860	• Water stored on ice and filtered within ≤24 hours     • Filters stored in commercial freezers or i ice filled coolers for 10 days or less (i.e. to allow time for shipping)	
	Air N <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub>			3 per lake total = 324		
Algae indicators	Chlorophyll a	<ul> <li>Water collected in opaque 1L HDPE bottle per analyte.</li> <li>Filtrate collected on Glass Fiber filter.</li> <li>Extract stored in glass vial</li> </ul>		QA/QC Total = ~130		
	phycocyanin			1 per lake + QA/QC Total = ~130		

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Analyte Group	Analyte	Filtered or unfiltered	Container and volume	Total number of samples	Preservation	Holding times
	,				<ul> <li>Upon receipt of ACESD, filters</li> <li>-20C for ≤60 d</li> </ul>	stored at
	microcystin	Unfiltered	20 mL amber glass vial	1 per lake + QA/QC Total = ~130	Less than 14 da several monti	-
	Temperature	NA, i	n situ	NA, in situ	NA, in situ	NA, in situ
	Conductivity	NA, i	n situ	NA, in situ	NA, in situ	NA, in situ
	рН	NA, i	n situ	NA, in situ	NA, in situ	NA, in situ
Sonde	Dissolved oxygen	NA, i	n situ	NA, in situ	NA, in situ	NA, in situ
	Chlorophyll a from sonde	NA, i	n situ	NA, in situ	NA, in situ	NA, in situ
T.11. 5. 6	Turbidity	NA, i	n situ	NA, in situ	NA, in situ	NA, in situ

Table 5. Sample containers and quantities assuming field duplicates will be collected for 10% of the unknowns.

### **B3. Sample Handling and Custody**

### B3.1 Sample labels

Site Kits and QA/QC kits (see F8. Surge EQUIPMENT AND SUPPLIES) will contain pre-labeled bottles for water chemistry and algal indicators and an additional labels to be affixed to foil packets containing the chlorophyll and phycocyanin filter (Figure 4). Unique samples will be identified by:

- analyte (Table 5):
  - 'dissolved nutrients', 'dissolved metals', 'TOC', 'total nutrients', 'chlorophyll', 'phycocyanin', 'microcystin'.
- QA/QC: 'duplicate' or 'blank' (QA/QC kit only)
- lake siteID: to be populated by field crew.
  - 7 digit alphanumeric code from siteID field in survey design file. Design file available in web map, the SuRGE GeoPlatform group, and the SuRGE documents library in SharePoint.
- Station siteID: to be populated by field crew.
  - alphanumeric code from lake specific survey design – water chemistry and algal indicators always collected from Index site
- Date: mm/dd/yy format
- depth: 'shallow' or 'deep'.
- Owner: Beaulieu 513-569-7842
- Matrix: "water", "filtered solids"
- Hazards: "nonhazardous" or "weak acid"
- Preservation: "-20c", "3 drops 2% HNO3", "2 drops 50% HCl and 4c", etc...

Gas sample vials provided in Base Kit (see F8. Surge EQUIPMENT AND SUPPLIES) will be pre-labeled with an alphanumeric code containing three ID fields (Figure 4C):

- a two digit letter code identifying the project
- a two digit numeric code identifying the year
- a four digit numeric code unique to each vial

Field crews
must populate
'station
siteID', 'Lake
siteID', and
'Date' fields
on sample
labels.

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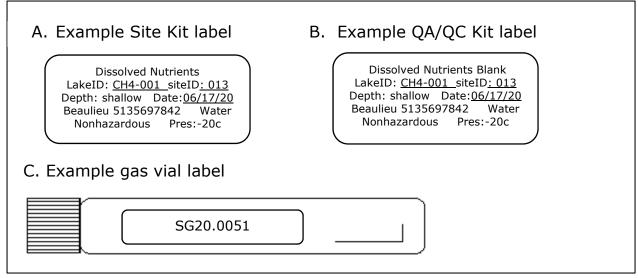


Figure 4. Example sample labels.

### B.3.2 Chain of custody

Chain of custody (CoC) forms will be populated for all water chemistry, algal indicator, and gas samples submitted for analysis (F9. Surge Water Chemistry Tracking Sheet, F10. Surge ALGAL INDICATOR Tracking Sheet, F11. Surge Gas sample Tracking Sheet). Separate Water Chemistry and Algal Indicator CoC forms will be populated for each lake. Gas samples from multiple lakes can be aggregated on one Gas Sample CoC. A hardcopy of the form (in a waterproof bag or plastic sleeve) will be shipped with the samples and an electronic version emailed to the laboratory.

#### **B.3.3 Shipping**

During extended field campaigns it may be difficult to maintain the algal indicator, dissolved nutrients, total nutrients, and TOC samples at the low temperatures required for preservation (Table 5). The default procedure for temperature sensitive samples is to either keep them on ice or in hotel room freezer; likely a combination of the two during extended field campaigns. The Field Crew Technical Lead may choose to ship temperature sensitive samples from the field, rather than trying to keep them frozen during extended sampling trips. FIELD SHIPPING IS ENTIRELY OPTIONAL. Based on past experience, water samples will remain partially frozen throughout long field days and are unlikely to be affected by freeze/thaw cycles. The chlorophyll and phycocyanin samples are likely to thaw, however. The Narragansett laboratory will conduct tests to determine the potential impact of freeze/thaw cycles on chlorophyll and phycocyanin.

Field crews are responsible for the cost of shipping samples to analytical laboratories. Analytical laboratories will cover the cost of returning empty coolers.

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#### B.3.3.1 Gas samples

Gas samples must be shipped via ground to avoid possible issues associated with changes in barometric pressure during flight. Samples should be sorted by sample type (e.g., AIR, dissolved gas (DG), Trap) within the provided trays and shipped within a suitable box (i.e. no refrigeration or cooler is necessary). A chain of custody form must be included in the shipping container and a copy e-mailed to the Gas Lab Technical Lead:

Ship gas samples to: USEPA ATTN: WHITE

ATTN: WHITE MS 585

26 Martin Luther King Dr. West

Cincinnati, OH 45268

Email: white.karenm@epa.gov

Phone: 513-569-7248

#### B.3.3.2 Water chemistry samples

ADA will analyze dissolved nutrients, total nutrients, and TOC samples at the ADA facility (no shipping required). ADA will ship dissolved metals to Cincinnati for analysis. All other field crewswill ship dissolved nutrients, total nutrients, TOC, and dissolved metals samples to Cincinnati for analysis. Glass TOC vials will be shipped within the provided bubble wrap bags.

Water chemistry samples must be shipped on ice via overnight delivery to Cincinnati. Place ice within sealed ziplock bags secured within a sealed cooler liner (e.g. thick plastic bag). Shippers will sometimes hold packages that are leaking water. A chain of custody form must be included in the cooler (in a plastic sleeve) and an electronic copy e-mailed to the Cincinnati Water Chemistry Technical Lead. Coolers cannot be received in Cincinnati on the weekends or federal holidays. Please ship accordingly.

Ship water chemistry samples to:

USEPA

ATTN: Venkatapathy

MS 483

26 Martin Luther King Dr. West

Cincinnati, OH 45268

Email: venkatapathy.raghuraman@epa.gov

Phone: 513-569-7077

#### B.3.3.3 Algal indicator samples

All field crews will ship the algal indicator samples to the Narragansett laboratory. Algal indicator samples must be shipped on ice via overnight delivery. Place ice within a sealed ziplock bags secured within a sealed cooler liner (e.g. thick plastic bag). Wrap glass microcystin vials in included bubble wrap. Shippers will sometimes hold packages that are leaking water. A Chain of Custody form must be included in the cooler (in a plastic sleeve) and an electronic copy e-mailed to the Narragansett Water Chemistry Lab Technical Lead. Coolers cannot be received on the weekends or federal holidays. Please ship accordingly.

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Ship algal indicator samples to:

**USEPA** 

ATTN: Hollister 27 Tarzwell Dr.

Narragansett, RI 02882 Email: <a href="mailto:hollister.jeff@epa.gov">hollister.jeff@epa.gov</a> Phone: 401-782-9655

### B.3.4 Paper records

Field crews will populate the paper records in section F. Appendix. The Field Crew Technical Lead is responsible for 1) maintaining the original records in accordance with Agency policy, 2) posting electronic scans of the paper records to the <u>SharePoint site</u> within 30 working days of returning to laboratory, and 3) entering data into data template by Dec. 1 of the year the data were collected. The data template can be found in the 'data' folder <u>SharePoint site</u>.

#### B.3.5 Electronic records

Data files will be downloaded from the greenhouse gas analyzer and GPS unit. These files must be transferred to sensor specific subfolders at the <u>SharePoint site</u> within 5 working days of returning to laboratory.

Additional electronic records will be generated from laboratory analysis. Water Chemistry and Gas Lab Technical Leads are responsible for depositing analytical data into analyte specific subfolders at the <a href="SharePoint site">SharePoint site</a>.

### **B.3.5.2** *Photos*

Photos (B1.3 Photos) will be uploaded to lake specific folders at the **SharePoint site**.

#### B.3.5.1 Greenhouse Gas Analyzer

The Los Gatos portable analyzer will create a datafile named following

"ggaYYYYMMDD\_f###.txt" where YYYYMMDD is the date, and f#### is a unique serial number that counts upward to provide up to 100,000 unique file names per day. One file should be generated each day the analyzer is used, and this file name must be recorded in F3. SuRGE GREENHOUSE GAS ANALYZER AND GPS DATA SHEET Within five working days after returning to laboratory, the data file must be downloaded and transferred to the <a href="SharePoint site">SharePoint site</a>. A copy of the file should be made and renamed following:

lgr.sampleDate.Lake.txt (i.e. lgr.03.20.2015.XXX.txt)

where XXX is the three-digit numeric component of the siteID field in the SuRGE survey design file. This file can be accessed through the <a href="web app">web app</a>, the <a href="SuRGE GeoPlatform group">SuRGE GeoPlatform group</a>, and the SuRGE documents library at <a href="SharePoint">SharePoint</a>.

The Picarro G2508 will create a data file named with the following convention:

- Example: CFHADS2007-20111222-000131-DataLog User.dat
- CFHADS: Instrument Serial Number
- 20111222: Year, month, and day of when file was started
- 000131: Hour, minute, and second of when file was started (using a 24-hour clock)

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One file should be generated each day the analyzer is used and this file name must be recorded in F3. SuRGE GREENHOUSE GAS ANALYZER AND GPS DATA SHEET. Within five working days after returning to laboratory, the data file must be downloaded and transferred to the <a href="SharePoint site">SharePoint site</a>. A copy of the file should be made and renamed following:

pic.sampleDate.Lake.txt (i.e. pic.03.20.2015.XXX.txt)

where XXX is the three-digit numeric component of the siteID field in the SuRGE survey design file. This file can be accessed through the <a href="web app">web app</a>, the <a href="SuRGE GeoPlatform group">SuRGE GeoPlatform group</a>, and the SuRGE documents library at <a href="SharePoint">SharePoint</a>.

#### B.3.5.2 GPS

A GPS will be used to track the boat location during the floating chamber deployment. The Base Kit will include a BadElf GPS Pro for this purpose, though field crews may use other devices at their discretion. Once data logging is complete, you can use the Bad Elf Utility app to save the recorded trip or connect the GPS to your computer with a USB cable and access the log files directly through your file explorer.

GPS data files will be named according to the following convention:

gps.sampleData.Lake (i.e., gps.03.20.2015.XXX)

where XXX is the three-digit numeric component of the siteID field in the SuRGE survey design file. This file can be accessed through the <a href="web app">web app</a>, the <a href="SuRGE GeoPlatform group">SuRGE GeoPlatform group</a>, and the SuRGE documents library at <a href="SharePoint">SharePoint</a>.

#### **B.3.5.2** Research Notebooks

The SuRGE documents library at <u>SharePoint</u> will be the central data repository. The SharePoint site contains a OneNote Research Notebook for the project (Notebook ID J-WECD-WMB-NB-2308). Edit rights to this notebook are currently limited to the Project and Field Crew Technical Leads. Field Crew Technical Leads may choose to manage an independent Research Notebook per ORD guidance (ORD PPM 13.2).

#### **B4. Analytical Methods**

### B4.1 Carbon dioxide, methane, nitrous oxide, argon, nitrogen, and oxygen

Dissolved gas samples stored in serum vials will be analyzed for  $CO_2$ ,  $N_2O$ , and  $CH_4$  via gas chromatography. Gas samples collected from the ebullition traps will be analyzed for oxygen, nitrogen, and argon, in additions to the gases identified above. All analysis will follow the latest version of SOP# J-WECD-WMB-SOP-1263.

Methane and CO<sub>2</sub> in the floating chamber headspace will be measured in real time using a Los Gatos Ultraportable Greenhouse Gas Analyzer or Picarro G2508. The systems use infrared detection and can make measurements as frequently as every second. Measurement precision

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decreases with increasing sampling frequency, however, and we will use a 10 second averaging period.

#### B4.2 Chlorophyll a

Chlorophyll samples will be processed in Narragansett following the SOPs listed below available in the SuRGE documents library at <a href="SharePoint">SharePoint</a>.

- SOP #J-ACESD-MAB-SOP-1425-0, Non-Acid Determination of Chlorophyll a Using a Turner Designs Trilogy Fluorometer
- SOP # J-ACESD-MAB-SOP-3950-0, Chlorophyll a Standard Curve for Turner Designs Trilogy Fluorometer

#### B4.3 Phycocyanin

Phycocyanin samples will be processed in Narragansett following SOP # J-ACESD-MAB-SOP-3949-0, *Determination of Phycocyanin Using a Turner Designs Trilogy Fluorometer*, available in the SuRGE documents library at <a href="SharePoint">SharePoint</a>.

#### B4.4 Microcystin

Microcystin samples will be processed in Narragansett following an SOP currently under development, to be made available in the SuRGE documents library at <a href="SharePoint">SharePoint</a>.

#### B4.5 All other analytes

The remaining analytes will be measured using standard operating procedures as detailed in Table 6. SOPs used in this project

The entire dissolved metals target analyte list for the Cincinnati lab can be seen in Table 7. Of those analytes, six are of interest to this project and are highlighted in yellow. Any calibration and QC verification troubleshooting will be focused on those six analytes. Data for all analytes will be appropriately flagged should other analytes found in these samples be of future interest.

Analyte	Laboratory	SOP ID	QA/QC
NO <sub>2.3</sub> -	ADA	K-GCRD-SOP-1151-0	See SOP
NH <sub>4</sub> <sup>+</sup>	ADA	K-GCRD-SOP-1151-0	See SOP
Reactive P	ADA	K-GCRD-SOP-1151-0	See SOP
TOC	ADA	K-GCRD-SOP-1165-0	See SOP
TN	ADA	K-GCRD-SOP-1151-0	See SOP
TP	ADA	K-GCRD-SOP-1151-0	See SOP
NO <sub>2.3</sub>	CIN	ESF-SOP-027	See SOP
NH <sub>4</sub> <sup>+</sup>	CIN	ESF-SOP-026	See SOP
Reactive P	CIN	ESF-SOP-029	See SOP

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Analyte	Laboratory	SOP ID	QA/QC
TOC	CIN	K-WID-SOP-3341-0	See SOP
TN	CIN	ESF-SOP-028	See SOP
TP	CIN	ESF-SOP-030	See SOP
Dissolved metals	CIN	SOP in development, based	See SOP
Dissolved illetais		on EPA method 200.8	
Temperature	NA	K-LRTD-SOP-1208-0	See SOP
Conductivity	NA	K-LRTD-SOP-1208-0	See SOP
turbidity	NA	K-LRTD-SOP-1208-0	See SOP
pН	NA	K-LRTD-SOP-1208-0	See SOP
Dissolved oxygen	NA	K-LRTD-SOP-1208-0	See SOP
Turbidity	NA	K-LRTD-SOP-1208-0	See SOP
In situ Chlorophyll a	NA	K-LRTD-SOP-1208-0	See SOP

Table 6. SOPs used in this project

DISSOLVED METALS ANALYTES	DETECTION
(Method: EPA 200.8)	LIMIT, µg/L
(Al) Aluminum	<mark>-0.004</mark>
(As) Arsenic	-0.004
(Ba) Barium	-0.001
(Be) Beryllium	-0.005
(CA) Calcium	<mark>-0.01</mark>
(Cd) Cadmium	-0.0003
(Cr) Chromium	-0.001
(Cu) Copper	-0.001
(Fe) Iron	-0.001
(K) Potassium	<mark>-0.3</mark>
(Li) Lithium	-0.005
(Mg) Magnesium	<mark>-0.005</mark>
(Mn) Manganese	-0.001
(Na) Sodium	<mark>-0.03</mark>
(Ni) Nickel	<mark>-0.001</mark>
(Pb) Lead	-0.002
(P) Phosphorus	-0.005
(Sb) Antimony	-0.003
(Si) Silicon	-0.02
(Sn) Tin	-0.001
(Sr) Strontium	-0.001
(S) Sulfur	-0.003
(V) Vanadium	-0.001
(Zn) Zinc	-0.0005

Table 7. Instrument dissolved metals analyte list: highlighted analytes are of interest for SuRGE project.

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### **B5. Quality Control**

### **B5.1 Laboratory Quality Metrics**

The SOPs referenced in Table 6 describe laboratory QA checks including standard curves, laboratory blanks, continuing calibration checks, and matrix spikes for lab-based measurements. Acceptance criteria and corrective actions are detailed for each SOP. Table 8 describes laboratory and field quality metrics for the greenhouse gas analyzer and the sonde measurement. See B5.2 Field Quality Metrics for more information.

Analyte	Quality metric	Frequency	Acceptance Criteria	Corrective Action
рН	post-deployment calibration check	Within 48 hours of the termination of field deployment	pH must be within 0.2 units of buffer	Recalibrate and flag field data
DO	post-deployment calibration check	Within 24 hours of the termination of field deployment	Within 5% of calculated value for water saturated air at the measured barometric pressure.	Recalibrate and flag field data
specific conductivity	post-deployment calibration check	Within 48 hours of the termination of field deployment	Within 15% of the standard value.	Recalibrate and flag field data
temperature	post-deployment calibration check	Within 48 hours of the termination of field deployment	Within 1C of value measured using a certified thermometer.	Recalibrate and flag field data
CH <sub>4</sub> and CO <sub>2</sub> via Los Gatos greenhouse gas analyzer	Field check with a mixed standard of 2.50 ppm and 400 ppm CH <sub>4</sub> and CO <sub>2</sub> , respectively.	Once per day of field use.	Reading must within 20% of true value.	Flag field data

Analyte	Quality metric	Frequency	Acceptance Criteria	<b>Corrective Action</b>
CH <sub>4</sub> and CO <sub>2</sub> via GGA	Record laser ring down times.	Once per day of field use.	No criteria but can be useful to track instrument condition.	NA
	Multipoint calibration check in the laboratory.	Beginning and end of field season.	Readings must within 15% of true value.	Recalibrate
	Multipoint calibration check in the laboratory.	Beginning and end of field season.	Readings must within 15% of true value.	Recalibrate
CH <sub>4</sub> , CO <sub>2</sub> , and N <sub>2</sub> O via Picarro greenhouse gas analyzer	Field check with a mixed standard of 2.50 ppm, 400 ppm, and 0.3 ppm CH <sub>4</sub> , CO <sub>2</sub> , and N <sub>2</sub> O standard, respectively.	Once per day of field use.	Reading must within 15% of true value.	Flag field data

Table 8. QA/QC checks not specified in the SOPs reported in Table 3

#### **B5.2 Field Quality Metrics**

Field duplicates and field blanks will be collected from one reservoir during each field outing. A field outing is defined as 'continuous days in the field, without returning to laboratory'. For example, sampling three waterbodies during a continuous 1.5 week trip would be considered a single 'field outing'. Similarly, sampling one lake over two days, then returning to laboratory, would also be considered a field outing.

Portable greenhouse gas analyzer performance will be checked with a field standard during every field outing.

#### B5.2.1 Field blanks

Field blanks for gas samples would require a cylinder of compressed gas be transported into the field. This is beyond the scope of the project and no field blanks will be collected for gas samples.

Field blanks for water chemistry and algal indicators will be prepared by transferring deionized water from a clean bottle (provided in Base Kit, see F8. Surge EQUIPMENT AND SUPPLIES**Error!**Reference source not found.) into the appropriate bottles. Field blanks will be treated identically to unknowns.

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No analyte should be present at concentrations greater than three times the minimum detection limit in the field blanks. If this criterion isn't met, but all lab QA/QC are within range, then the field blanks were likely contaminated during sampling. The corrective action is to evaluate cleaning procedures for deficiencies.

#### B5.2.2 Field duplicates

Field duplicates will be collected for all algal indicators and water chemistry analytes, except those measured *in situ*. These duplicates will be used to evaluate the sampling/environmental variability of the analyte concentrations. No acceptance criteria or corrective action will be associated with this quality metric.

All dissolved gas and air samples will be collected in triplicate. Passive trap gas samples will be collected in triplicate when sufficient gas is available. These samples will be used to evaluate sampling variability for these analytes. No acceptance criteria or corrective action will be associated with this quality metric.

#### B5.2.3 Field standards

At the end of each field day the portable greenhouse gas analyzer calibration should be checked with an analytical standard. This is accomplished by interfacing the instrument inlet tubing to a compressed gas cylinder via a regulator. The regulator should be set to approximately 5 psi and the gas allowed to flow through the analyzer until the readings stabilize (approximately 1 minute). The concentration and associated performance specifications should be recorded in F12. LOS GATOS GREENHOUSE GAS ANALYZER QA/QC SHEET or F13. PICARRO GREENHOUSE GAS ANALYZER QA/QC SHEET. Acceptance criteria for the calibration check is +/- 20% of known concentration. If the QA/QC check fails on a Los Gatos instrument, check the spectra and adjust the lasers if needed. See user manual in SuRGE documents library at SharePoint for more information.

This procedure has the added benefit of drying the measurement cell prior to instrument shut down. If, during shut down, the water vapor mixing ratio is within 20% or 5% of the saturation value (Table 9) for the LGR and Picarro, respectively, water can condense in the measurement cell and potentially affect precision and bias. Based on previous deployments, it is not uncommon for water vapor to exceed the saturation point when the chamber is floating on the water surface, though values typically fall when the chamber is pulled into the boat. Measurement cells can also be dried by passing air through an in-line desiccant column prior to being delivered to analyzer.

		Saturation mixing ratio	Acceptable	level (ppm)
T (deg F)	T (deg C)	(ppm)	LGR	Picarro
32	0	6,000	4,800	5700
41	5	8,500	6,800	8075
50	10	12,100	9,680	11495
59	15	16,800	13,440	15960
68	20	23,000	18,400	21850
77	25	31,200	24,960	29640
86	30	41,800	33,440	39710
95	35	55,400	44,320	52630
104	40	72,600	58,080	68970

Table 9. Maximum  $H_2O$  mixing ratio for shut down of Los Gatos and Picarro analyzers as a function of ambient temperature.

### B6/B7. Instrument/Equipment Calibration, Testing, Inspection, Maintenance

#### B7.1 Greenhouse gas analyzer

All greenhouse gas analyzers (Picarro and LGR models) will have the factory calibration tested against 10-point curve in the Cincinnati gas lab per SOP 1273-1 'Technical SOP for the 10-point Calibration Verification of the Los Gatos Research Ultraportable Greenhouse Gas Analyzer (LGR-UGGA)' at the beginning and end of the field season (SOP available at ORD intranet site and SuRGE documents library at SharePoint). Per vendor recommendation, data will be corrected for any deviation from a 1:1 relationship between measured and known values, rather than changing the instrument calibration. Data correction will be performed by the Project Technical Lead.

LGR greenhouse gas analyzers are covered by warranties that include an annual 'remote health check' by the vendor. This preventative maintenance will be conducted near the beginning of each field season.

#### **B7.2** Thermometers

The Base Kit will include a new digital thermometer and NIST traceable calibration certificate. The calibration certificate must be renewed annually. This can be done by each field crew following CESER SOP K-LRTD-SOP-1172-1, "Thermometer Calibration". Alternatively, field crews may return thermometers to Cincinnati for calibration at the CESER Cincinnati Metrology Laboratory. SOP available at <a href="ORD intranet site">ORD intranet site</a> and SuRGE documents library at <a href="SharePoint">SharePoint</a>.

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#### **B7.3** Barometers

Calibrations on Field Crew supplied barometers must be checked annually. Most field crews will use YSI brand barometers with factory calibration tolerance of ±1mm Hg. If the Field Crew Technical Lead cannot check the barometer calibration locally, this service can be performed through the CEMM QA office in Cincinnati. Contact the SuRGE project QA/QC officer for details.

#### **B7.4 Cleaning**

Several durable items in the Base Kit (see F8. Surge EQUIPMENT AND SUPPLIES, B8.2 Base kit) require cleaning between uses. Items not specifically mentioned in 'B7.4.1 Water chemistry' and 'B7.4.2 Algal indicators' do not need cleaning between uses.

#### *B7.4.1 Water chemistry*

The Base Kit (see F8. Surge EQUIPMENT AND SUPPLIES, B8.2 Base kit) includes five syringes for collecting dissolved nutrients and dissolved metals. Syringes must be cleaned with a laboratory detergent (e.g. Alconox or equivalent), soaked in an acid bath of 5% ACS trace-element grade HCl for 30 minutes, and rinsed 3 times with DI water between uses.

#### *B7.4.2 Algal indicators*

The Base Kit (see F8. Surge Equipment and Supplies, B8.2 Base kit) includes three opaque 1 L bottles for chlorophyll sampling (i.e. one bottle for unknowns, one for blanks, and one for duplicates), three opaque 1 L bottles for phycocyanin sampling (i.e. one bottle for unknowns, one for blanks, and one for duplicates), and one filter tower assembly. During extended field trips it is sufficient to clean this equipment using tap water in the hotel (or equivalent) between uses. Equipment should be washed in a laboratory detergent (e.g. Alconox or equivalent) and rinsed with DI water upon return to laboratory.

#### B7.4.3 Watercraft and Equipment

The watercraft and equipment that are deployed in reservoirs may become contaminated with invasive species. A variety of preventative measures may be taken to minimize the transfer of these "hitchhikers" among reservoirs as teams move from site to site. SuRGE strongly recommends the following minimum precautions:

**Clean**: the trailer, boat hull, motor and equipment that were deployed will be cleaned. Use provided scrub brush and scrubbing pad to remove all visible plants, animals and mud.

**Drain**: all sources of stored water will be drained. Remove the boat plugs, drain all bilge, live well and motor water.

**Dry**: boat, motor and trailer will be dried with provided shammy towel, or equivalent, unless the boat will remain out of water for at least five days.

If possible, pressure spraying boat and equipment (e.g., manual car wash) may further ensure non-native species are removed.

Field Crew Technical Leads may optionally choose to disinfect watercraft and equipment. Per New York State <u>guidance</u>, SuRGE recommends one of the following disinfection methods:

- hot water greater than 120°F
- 2% bleach (10% if whirling disease is present; caution, corrosive to aluminum)
- 200ppm potassium chloride (2 teaspoons/2 gallons water).

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SuRGE will include KCl pellets in Base Kit (Base Kit; F8. SuRGE EQUIPMENT AND SUPPLIES) to be optionally used for disinfection. Anchors and rope could be dipped in KCl solution; larger pieces of equipment (including boat hull) could be wiped with solution.

Teams should be aware of local regulations concerning watercraft and equipment regarding aquatic invasive species and the presence of invasive species in reservoirs they visit. The following are helpful resources:

https://stopaquatichitchhikers.org/

https://www.invasivespeciesinfo.gov/subject/watercraft-inspection-and-decontamination-programs

http://nsglc.olemiss.edu/projects/model-legal-framework/files/state-comparison-revised.pdf

#### **B8.** Inspection/Acceptance of Supplies and Consumables

See F8. Surge Equipment and Supplies for a complete equipment list. The Project Technical Lead is responsible for ensuring that supplies shipped to field crews contain the listed equipment and supplies and that the equipment and supplies are of the required quality for collection of samples and field measurement. The Technical Leads for analytical labs in Cincinnati, Ada, and Narragansett are responsible for ensuring supplies and consumables meet project quality standards. Consumables are inspected when received. Consumables with expiration dates will be used prior to expiration unless recertified or otherwise justified in research records.

#### B8.1 Greenhouse gas analyzer kit

USEPA/ORD/CEMM/WECD/WMB (Cincinnati) will provide each field crew with a CO<sub>2</sub>/CH<sub>4</sub> analyzer and floating chamber to measure CO<sub>2</sub> and CH<sub>4</sub> diffusive emission rates. The analyzer will be either a Los Gatos UltraPortable Greenhous Gas Analyzer (UGGA) or a Los Gatos Microportable Greenhouse Gas Analyzer (MGGA). The Cincinnati field crew will use a Picarro G2308. The Los Gatos analyzers are controlled via VNC Viewer freeware running on iOS, android, or PC. An iOS iPad will be provided with each Los Gatos instrument, but local field crews may use other devices if preferred. See F8. Surge Equipment and Supplies for list of kit contents.

#### B8.2 Base kit

The Base Kit is comprised of the subset of durable equipment and supplies needed to execute the survey. Each field crew will be supplied a Base Kit by USEPA/ORD/CEMM/WECD/WMB (Cincinnati), unless the field crew chooses to supply their own Base Kit. See F8. Surge EQUIPMENT AND SUPPLIES for list of kit contents.

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#### B8.3 Site kit

A Site Kit contains the subset of consumable supplies (i.e., items that require replacement after use) and will be provided by USEPA/ORD/CEMM/WECD/WMB (Cincinnati). The site kit will contain all sample bottles necessary for sampling a single lake. Crews should consider having at least one additional site kit available as a spare should any supplies be lost. See F8. Surge EQUIPMENT AND SUPPLIES for list of kit contents.

### B8.4 QA/QC kit

One field duplicate and field blank will be collected for each water chemistry and algal indicator analyte (TOC, TN/TP, NO2.3/NH4+/SRP, metals, chlorophyll, phycocyanin, microcystin) during each 'field outing'. A field outing is defined as 'continuous days in the field, without returning to laboratory'. For example, sampling three waterbodies during a continuous 1.5 week trip would be considered a single 'field outing'. Similarly, sampling one lake over two days, then returning to laboratory, would also be considered a field outing. See F8. Surge Equipment and Supplies for list of kit contents.

USEPA/ORD/CEMM/WECD/WMB (Cincinnati) will distribute QA/QC kits to field crews based on anticipated sampling schedule.

#### **B8.5 Field Crew Supplied Items**

The field crew will also supply items for the survey. These items include general field equipment (i.e., printed data sheets, pens), limnological equipment (i.e. multi-parameter probe), and boat equipment. See F8. Surge EQUIPMENT AND SUPPLIES for items the field crew will need to provide.

#### **B9. Non-direct Measurements**

#### **B10.** Data Management

#### B10.1 Data analysis workflow

The SuRGE documents library at <u>SharePoint</u> will be the central data repository. Field Crew Technical Leads will be responsible for uploading electronic data per sections 'B.3.4 Paper records' and 'B.3.5 Electronic records'. The Project Technical Lead will be responsible for organizing a collaborative and reproducible data submission and analysis workflow. This will be accomplished by 1) using R for data analysis and visualization, 2) using a public repository under the EPA's institutional account for sharing code, and 3) using git to establish version control over code. Additional benefits of this workflow are 1) all EPA data will be accessible to collaborators (including outside collaborators), but not the general public, and 2) all electronic resources will be protected from loss via institutional back-up safeguards.

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The Project Technical Lead will lead most aspects of data analysis leading to a final aggregated data set. This will include 1) writing code to read in field and laboratory data, 2) calculate derived quantities from measured data (e.g., diffusive emission rates from gga data, dissolved gas concentrations from gas chromatograph data), 3) aggregate across field duplicates, 4) track QA/QC flags, and 5) upscale point measurements to reservoir-scale estimates of mean and variance.

The final aggregated data set will be used to generate a national-scale estimate of CH<sub>4</sub> and CO<sub>2</sub> emissions from U.S. waterbodies. This effort will be conducted collaboratively with all interested SuRGE team members. We have identified several approaches for upscaling our measurements to the nation including 1) classical survey design calculations, 2) using the data train a predictive model for estimating emissions from all U.S. reservoirs, and 3) a combination of the two. Survey design calculations will be executed using function in the spsurvey library in R and features of the SuRGE probabilistic survey design. We will likely explore a variety of modeling approaches including machine learning algorithms, generalized linear models, generalized additive models.

#### B10.2 Laboratory specific data management

Technical Leads for the Water Chemistry and Gas labs are responsible for ensuring that reported data meet the relevant QA/QC criteria, per the SOPs, or are flagged appropriately. Data should be uploaded to SharePoint per 'B.3.5 Electronic records'. A variety of reporting formats are accepted, as long as reports are clear with respect to analytes, flags, and concentration units.

#### C. ASSESSMENTS AND OVERSIGHT

#### C1. Assessments and Response Actions

#### **C2.** Reports to Management

The Project Technical Lead will be responsible for reports to management. These will likely come in the form of informal briefings to staff in the Office of Air and Radiation, the National Program Director and associated staff in the Air and Energy national research program, and management within the Center for Environmental Measurement and Modeling.

Tangible products from this research will include an estimate of GHG emissions from US reservoirs for inclusion in the Inventory of US GHG Emissions and Sinks and at least one journal article in a peer reviewed journal.

The Project Technical Lead will organize periodic project meetings, primarily via Skype, and will look for opportunities to conduct in-person meetings. In-person meetings will most likely be

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attached to pre-existing meetings that SuRGE team members plan to attend such as conferences.

#### D. DATA VALIDATION AND USABILITY

### D1/D2. Data Review, Verification, and Validation/Verification and Validation Methods

Problems with data integrity are most likely to arise when transcribing paper records to electronic format (see B.3.4 Paper records). To address this issue, Field Crew Technical Leads will be responsible for ensuring that a minimum of 10% of entered data is checked for accuracy by Research Support Staff. The Project Technical Lead will develop additional QA/QC checks designed to detect egregious data entry issues (e.g., misplaced decimal place, incorrect units).

Data problems can also arise due to coding errors. To address this issue, SuRGE team members will be encouraged to clone the Github repository (B10.1 Data analysis workflow) and run/inspect the code. Code used for upscaling our measurements to the nation must be run by at least two team members and the results compared for inconsistencies.

#### D3. Analysis and Reconciliation with User Requirements

The Project Technical Lead will work closely with Office of Air and Radiation (OAR) to ensure the data are reported in a format consistent with their intended use. Formats will include a peer-reviewed manuscript describing the main project results and an emission rate estimate reported per the standardized reporting requirements for Inventory of GHG Emissions and Sinks as dictated by the United Nations. This will include a brief description of how the data were generated and aggregated for use in the inventory. OAR will submit the report for additional national and international review.

#### E. References

Livingston, G. P., and G. L. Hutchinson Enclosure-based measurement of trace gas exchange: applications and sources of error, in *Methods in Ecology: Biogenic trace gases: Measuring emissions from soil and water*, edited by P. A. Matson and R. C. Harriss, pp. 14-51, Blackwell Science LTD, Oxford.

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# F. Appendix

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# **F1. Surge Sampling Event Summary**

Lake siteID:		Sampling Dates	s:		Timezone:		
INDEX siteID:			IN	NDEX site eval st	atus:		
siteID	¥Eval status	siteID <sup>¥</sup> Ev	val status	siteID	Eval status	siteID	¥Eval status
¥Eval Status: Т	S (Target San	npled), PI (Physic	ally inacce	essible), NT (Nor	n-Target), NS	(Target No	ot Sampled).
General notes	(weather, al	gae bloom, etc):					
Name (print):		Signature:				Date:	

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### **F2. SURGE GAS TRAP DATA SHEET**

Lake siteID:		Time zone	::	Year:		Exetainer code prefix	<b>,</b> .	
Station	Lat	Long	Deployment time/date	Retrieval time/date	Volume recovered		digits of Ex	ketainer
siteID	XX.XXXXXX	xxx.xxxxxx	hh:mm dd/mm	hh:mm dd/mm	(mL)		codes	
Commen	ts.							
Commen								
Name (print)		Signa	ture:			Date:		

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#### F3. SURGE GREENHOUSE GAS ANALYZER AND GPS DATA SHEET

Lake siteID:											
Sample Date:							1				
Time zone use	d for data e	entry below	<b>/</b> :								
Gas analyzer fi	le name:										
*gps file name	(if availabl	e):									
gps time zone:											
*GPS unit will collect	oositional data tl	nroughout all cha	ambe	er dep	ployme	ents					

<sup>†</sup>Water \*CH<sub>4</sub> and CO<sub>2</sub> Chamber volume profile checked? Station siteID Chamber start time temperature (°C) graduation YES□ No□ YES□ No□ No□ YES□ YES□ No□ Name (print): Signature: Date:

<sup>\*</sup>CH<sub>4</sub> should steadily increase during chamber deployment. CO<sub>2</sub> may increase or decrease, depending on algae productivity.

<sup>+</sup>Only record water temperature if not recording 'shallow' sonde data.

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### F4. Surge sonde data sheet for index site depth profile

Lake si	teID:			Index s				_Index si	ite dep	th (m):		[	ate:		
Depth(m) xx.x	Temp (C) xx.x	DO (mg/L) xx.x	sp.Cond (μs cm <sup>-1</sup> ) xx	pH xx.x	Chl a (ug/L) xx.x	Turbidity (NTU) xx.x	Flags	Depth(m)	Temp	DO (mg/L) xx.x	sp.Cond (μs cm <sup>-1</sup> ) xx	pH xx.x	Chl a (ug/L) xx.x	Turbidity (NTU) xx.x	Flags
XXIX	AAIA	XXX	, AA	AAA	AAAA	AAAA	11053	AAIA	XXX	XXIX	, , ,	АЛЛ	AAA	XXIX	riago
								_							
								-							
								-							
								-							
								_							
-													-		
Flag C	ommer	nts													
	es: k = No n commer			bservatio	on made,	U = suspe	ect mea	surement o	r observa	ation, F1,	F2, etc = fl	ags define	ed by field	l crew. Ex	plain
Name (print):						Signat	ure:					Dat	e:		

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# F5. Surge sonde data sheet for deep and shallow measurements

Lake s	iteID:_								Date:								
				SHALLO	OW MEAS	UREMEN	ΓS					DEE	P MEASUR	REMENTS			
Station siteID	Site depth(m) xx.x	Sample depth(m) xx.x	Temp (C) xx.x	DO (mg/L) xx.x	sp.Cond (μs cm <sup>-1</sup> ) xx	pH xx.x	Chl a (ug/L) xx.x	Turbidity (NTU) xx.x		Sample depth(m) xx.x	Temp (C) xx.x	DO (mg/L) xx.x	sp.Cond (μs cm <sup>-1</sup> ) xx	pH xx.x	Chl a (ug/L) xx.x	Turbidity (NTU) xx.x	Flag
Flag	Comm	ents															
		o measure ents secti		r observ	ation ma	de, U = s	suspect r	measure	ment	or observ	/ation, F	1, F2, etc	= flags d	efined b	y field cre	ew. Expla	ain
	(print)							Sign	atur	e:				Dat	e:		
														_ [			

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### F6. Surge Chlorophyll/Phycocyanin sample prep data sheet

Collection date	Lake siteID	Station siteID	*Sample Type	†Analyte	Filter date	Volume filtered (mL)
*unknown (UI	NK), duplicate (D	OUP), or blank (E	BLK) <sup>†</sup> Chloroph	yll or phycocya	nin	
Name (print):		Siį	gnature:		Date:	

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# F7. SURGE DISSOLVED GAS AND AIR DATA SHEET

Lake siteID:		Index siteID:			Date:			Exetainer code prefix:	
		DI	SSOLVED (	GAS S	AMPLII	NG [	DATA	<b>P</b> C	
*Sample depth	Sample depth (m)	of Exc	our digits etainer ode	equi	idspaco libratio peratur (C)	on	No	tes/Comm	ents
shallow	~0.1m								
shallow	~0.1m								
shallow	~0.1m								
deep									
deep									
deep									
under wat	samples colle er surface. T bles collected	his depth	could exc	eed 10	cm if	wav	es are prese	ent. If site o	lepth <4m,
			AIR SA	AMPLI	NG DA	TA			
BP (mm H	Air Temp g) (C		Last	t four (	digits o	of at	mospheric a	nir Exetaine	r odes
Name (print):			Signature	e: 				Date:	

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### **F8. Surge Equipment and Supplies**

### **Greenhouse Gas Analyzer Kit**

USEPA/ORD/CEMM/WECD/WMB (Cincinnati) will provide each field crew with a portable greenhouse gas analyzer. Analyzers will be returned to Cincinnati at end of each field season.

Greenhouse Gas Analyzer Item	Quantity	Protocol
Picarro G2308, Los Gatos UGGA, or Los Gatos M-GGA	1	Diffusive emissions
Analyzer battery	1	Diffusive emissions
Battery to analyzer cable	1	Diffusive emissions
Charger for analyzer battery	1	Diffusive emissions
AC power cable for analyzer (wall outlet to analyzer)	1	Diffusive emissions
Analyzer maintenance kit	1	Diffusive emissions
Inlet filter (Los Gatos instruments only)	1	Diffusive emissions
Field standard, regulator, and tubing for analyzer	1	Diffusive emissions
Zero air, regulator, and tubing for analyzer (Picarro only)	1	Diffusive emissions
Float chamber and tubing	1	Diffusive emissions
iPad with ArcGIS Collector and LGR software	1	Diffusive emissions and locating sampling sites

#### **Base Kit**

USEPA/ORD/CEMM/WECD/WMB (Cincinnati) will provide each field crew with a compete Base Kit. Field crews will keep the Base Kit through the duration of their involvement in the project.

Base Kit Item	Quantity	Protocol
Pre-evacuated and labeled Exetainers in test tube racks (up to 69 per lake)	Dependent upon number of sites a crew plans to sample	Dissolved gas and air sampling
Scrub brush	1	Cleaning equipment
Potassium chloride (KCl) pellets	TBD	Cleaning equipment/boat
Abrasive scrubbing pad	1	Cleaning boat
Shammy towel	2	Cleaning boat
Nut driver for hose clamps	1	Passive traps

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Adjustable wrench for quick links	1	Passive traps
Extra quick links	5	Passive traps
Extra brass rings	5	Passive traps
Teflon tape	1 role	Passive traps
Funnels with eyelets	22	Passive traps
Quick links (four per set of uprights)	66	Passive traps
Tall (32") upright sets with two brass rings and one quick link per set.	17	Passive traps
Short (15") upright sets with two brass rings and one quick link per set.	5	Passive traps
Buoys	22	Passive traps
Rope kit	1	Passive traps
Anchors	22	Passive traps
140 mL syringe with one- way stopcock	6	Dissolved gas sampling
140 mL syringe, no stopcock	1	Passive trap sampling
30 mL syringe with one- way stopcock	6	Passive trap and air sampling
Needle, 27 gauge	100	Passive trap, dissolved gases, air samples
250 mL bottle for Sharps box	1	Needle disposal
50 mL centrifuge tube	1	Dissolved gas sampling
Thermometer		
1L graduated cylinder (plastic)	1	Chlorophyll/phycocyanin
Opaque 1L bottle	6	Chlorophyll/phycocyanin
1 L bottle	2	Field blank

Squeeze bottle	1	Rinsing filter tower
Acid washed 140 mL syringe for chemistry samples	5	Water chemistry
Nitrile gloves	1 box of S/M/L	Collecting water chemistry, processing algal indicator
Hand or battery powered vacuum pump with gauge	1	Chlorophyll
Vacuum flask	1	Chlorophyll
Filter assembly	1	Chlorophyll
0.7μm glass fiber filters	50	Chlorophyll
Forceps	1	Chlorophyll
Aluminum foil	1 roll	Chlorophyll
Specimen bag	50	Chlorophyll
Bluetooth GPS	1	Locating sites

#### Site Kit

The Site Kit contains consumables used at each waterbody. USEPA/ORD/CEMM/WECD/WMB (Cincinnati) will provide each field crew with one Site Kit per waterbody, based on anticipated sampling schedules.

Site Kit Item	Quantity	Protocol
40 mL TOC vial	2	Water chemistry (TOC)
30 mL HDPE vial	4	Water chemistry (TN/TP, NO2.3/NH4+/SRP)
60 mL HDPE vial	2	Water chemistry (metals)
Disposable syringe filter for chemistry	4	Water chemistry (metals, NO2.3/NH4+/SRP, QA/QC)

#### QA/QC Kit

One field duplicate and field blank will be collected for each water chemistry analyte (TOC, TN/TP, NO2.3/NH4+/SRP, metals) during each 'field outing'. A field outing is defined as 'continuous days in the field, without returning to laboratory'. For example, sampling three waterbodies during a continuous 1.5 week trip would be considered a single 'field outing'. Similarly, sampling one lake over two days, then returning to laboratory, would also be considered a field outing.

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USEPA/ORD/CEMM/WECD/WMB (Cincinnati) will distribute QA/QC kits to field crews based on anticipated sampling schedule.

QA/QC Kit Item	Quantity	Protocol		
40 mL TOC vial	2	Water chemistry (TOC): blank and field duplicate		
30 mL HDPE vial	4	Water chemistry (TN/TP, NO2.3/NH4+/SRP): blank and field duplicate		
60 mL HDPE vial	2	Water chemistry (metals): blank and field duplicate		
Disposable syringe filter for chemistry	3	Water chemistry (metals, NO2.3/NH4+/SRP): blank and field duplicate		

### **Field Crew Supplied Items**

Field Crew Supplied Item	Quantity	Protocol
Multiparameter sonde with probes for optical DO, chl a, pH, turbidity, temperature and conductivity. Load with fresh batteries.	1	Site physicochemical characterization
Calibration cups and standards for multiparameter sonde	1	Sonde calibration
Weighted sonde deployment cap	1	Site physicochemical characterization
Sonde communication cable. Crews may choose to procure a cable sufficiently long to conduct depth profiles. Alternatively, depth profiles may be logged internally without use of communication cable.	1	Site physicochemical characterization
Sonde display unit with barometer	1	Site physicochemical characterization
Van Dorn bottle, or similar	1	Water chemistry

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Depth Finder (hand-held or boat mounted sonar)	1	Site physicochemical characterization	
Cooler with ice for field use	1	Water chemistry	
Cooler with ice for shipping	2	Water chemistry	
2L laboratory grade deionized water for field blank	1	QA/QC	
500mL distilled water (e.g. bottled water from gas station)	1	Algal indicator	
Water resistant paper		Data sheets	
Pen	1	Data sheets	
Permanent marker (fine tip, for labels)	1	General	
<b>OPTIONAL:</b> 5-gallon bucket for equipment disinfection	1	KCl solution for cleaning boat/equipment between lakes	
<b>OPTIONAL:</b> Field laptop with ArcPad and software for GHG analyzer.	1	Locating sites	
<b>OPTIONAL:</b> Cell phone for site pictures. Can use provided iPad.	1	Site description	
OPTIONAL: GPS unit	1	Site location	

# **Boat Equipment List**

Suggested boat equipment

Item
Personal Flotation Device (see local requirements)
SHEM approved boat safety bag
Boat anchor w/100 to 200 foot lines (line in a bucket or spool)
Paddle
Push pole for shallow waters
Wheel lug nut wrench, spare tire, and jack (probably use vehicle jack)
Gas and oil can
Spare prop and shear pin
Boat plug (extra)
Bow/stern lights

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Fire extinguisher

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### **F9. SURGE WATER CHEMISTRY TRACKING SHEET**

SuRGE \	WATER	CHEMI	STRY SAM	PLE TR	RACKING SHEET	
		SHIPF	PING INFORMAT	TION		
Sender:				ender Pho	one:	
Shipped by: O FedEx O	UPS OOt	her:				
Tracking Number:				Date Sen	t:	
		LAI	KE INFORMATIO	)N		
Lake siteID:				Crew:		
Dates Collected:						
		SAM	PLE INFORMAT	ION		
ROUTINE SAMPL			DUPLICATES		BLANKS	
Sample type	Collected?	Sa	ample type	Collected?	Sample type	Collected?
Dissolved nutrients - deep		Dissolved nuti	rients - deep		Dissolved nutrients - deep	
Dissolved nutrients - shallow		Dissolved nuti	rients - shallow		Dissolved nutrients - shallow	
Dissolved metals - deep		Dissolved met	Dissolved metals - deep		Dissolved metals - deep	
Dissolved metals - shallow		Dissolved met	tals - shallow		Dissolved metals - shallow	0
TOC - deep		TOC - deep			TOC - deep	
TOC - shallow		TOC - shallow			TOC - shallow	
Total nutrients - deep		Total nutrient	s - deep		Total nutrients - deep	
Total nutrients - shallow		Total nutrient	s - shallow		Total nutrients - shallow	
Water Chem	nistry Lab				NOTES	
USEPA ATTN: Venkatapathy MS 486 26 West Martin Luthe Cincinnati, OH 45268 Phone: 513-569-707 Email: Venkatapathy.rag	7	@epa.gov	broke):  RECEIVED	nems (e.g. III	o deep samples collected because V	an DOIT
Name:		Signature:			Date:	

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### F10. SURGE ALGAL INDICATOR TRACKING SHEET

SuR	GE ALGAL	INDICA	TOR SAM	PLE TR	ACKING S	HEET	
		SHIPE	ING INFORMA	TION			
Sender:		311111		ender Pho	one:		
Shipped by: O FedE	x o UPS o Ot	her:					
Tracking Number:				Date Sen	t: 		
		LAI	(E INFORMATI	ON			
Lake siteID:			-	Crew:			
Date Collected:							
		SAM	PLE INFORMA	TION			
ROUTIN		Carrage to man	DUPLICATES	Callantada		BLANKS	II = =4 = =1°
Sample type	Collected?	Sample type		Collected?	Sample type	Col	llected
chlorophyll		chlorophyll			chlorophyll		
phycocyanin		phycocyanin			phycocyanin		
microcystin		microcystin			microcystin		
Water C	hemistry Lab				NOTES		
USEPA ATTN: Hollister 27 Tarzwell Drive Narragansett, RI Phone: 401 782 9 Email: hollister.je	655		Please note any pro	blems (e.g. m	icrocystin bottle bro	oke):	
			RECEIVED				
Name:		Signature:			Date:		

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### **F11. SURGE GAS SAMPLE TRACKING SHEET**

SHIPPING INFORMATION									
Sender:			Sender Pho	Sender Phone:					
Shipped by: O FedE	x OUPS OOther								
Tracking Number: Date Sent:									
hip to : USEPA, ATTN: WHITE, 26 Martin Luther King West (MS 585), Cincinnati, OH 45268									
		ov, phone: 513-569-7	7248						
GAS VIAL INFORMATION									
EXETAINER CODE	SAMPLE TYPE (AIR, DG, TRAP)	EXETAINER CODE	SAMPLE TYPE (AIR, DG, TRAP)	EXETAINER CODE	SAMPLE TYPE (AIR, DG, TRAP)				
EXETAINER CODE	(AIN, DG, TNAP)	EXETAINER CODE	(AIR, DG, TRAP)	EXETAINER CODE	(AIN, DG, TRAP)				
		RECE	IVED						
Name:	Sig	gnature:	Date:						

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# F12. LOS GATOS GREENHOUSE GAS ANALYZER QA/QC SHEET

Instrument mod	el (UGGA or MG	GA):		Instrument serial	number:		
					Cali	bration check	
		Laser A τ	Laser B τ	Cal check start	Cal check 6	end CH <sub>4</sub> after 1	CO <sub>2</sub> after 1
Date	Lake siteID	(ringdown time)	(ringdown time	) time	time	minute	minute

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# F13. PICARRO GREENHOUSE GAS ANALYZER QA/QC SHEET

		Calibration check								
		1-minute mean 1-minute precision								
		Cal check	Cal check							Measurement
Date	Lake siteID	start time	end time	CH <sub>4</sub> (ppm)	CO <sub>2</sub> (ppm)	N <sub>2</sub> O (ppb)	CH <sub>4</sub> (ppm)	CO <sub>2</sub> (ppm)	N₂O (ppb)	interval